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Multiphoton Lithography of Nanocrystalline Platinum and Palladium for Site-Specific Catalysis in 3D Microenvironments

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Supporting Information Placeholder

ABSTRACT: Integration of catalytic nanostructured platinum and palladium within 3D microscale structures or fluidic environments is important for systems ranging from micropumps to microfluidic chemical reactors and energy converters. We report a generalizable and straightforward route to fabricate microscale patterns of nanocrystalline platinum and palladium using multiphoton lithography (MPL). These materials display excellent catalytic, electrical, and electrochemical properties and we demonstrate high resolution integration of catalysts within 3D-defined microenvironments to generate directed autonomous particle and fluid transport.

Platinum and palladium catalysts are crucial for a broad range of existing and emerging chemical, biological, and technological applications and so consequently, substantial recent work has been aimed at understanding and improving their function and efficiency and reducing their consumption/utilization via nanostructuring.¹ Despite progress towards directed synthesis of a wide variety of platinum and palladium nanostructures and alloys, there are few reported strategies for integration of these catalysts within nano or micro-scale platforms. Specifically, abilities to dictate catalysis within microfluidic systems are crucial for the success of lab on chip devices which rely on well-defined

catalyst/substrate interactions for improved efficiency, portability, and cost.² Increasingly microfluidic designs incorporate 3D channel geometries^{3,4} and therefore development of a strategy for precise positioning of catalysts within 3D microfluidics should prove enabling for a wide range of technologies including autonomously powered microfluidics, diagnostics, microreactors, and sensors as well as energy generation, conversion, and storage applications.⁵⁻⁷

Platinum, palladium and rhodium have been incorporated into a microfluidic hydrogenation reactors via processes such as sputtering,^{8,9} and recently Xu *et al.* used direct laser writing to pattern catalytic and SERS active silver microflowers within a microfluidic channel.¹⁰ Despite these examples, the scope of catalyst printing for microreactors remains limited and successful integration of catalysts such as Pt and Pd within 3D microfluidics has not been demonstrated.

Here we describe a straightforward procedure to integrate arbitrary micropatterns of nanostructured Pt and Pd within 3D fluidic architectures using multiphoton lithography (MPL), an intrinsically 3D direct-write technique.^{11,12} These MPL-deposited Pt and Pd materials are composed of polycrystalline metallic nanoparticles that show excellent electronic, electrochemical, and catalytic properties. We show that site-specific H₂O₂ decomposition catalyzed by MPL-directed Pt can be used to drive directed fluid flow in three dimensions upon integration within appropriately designed 3D structural

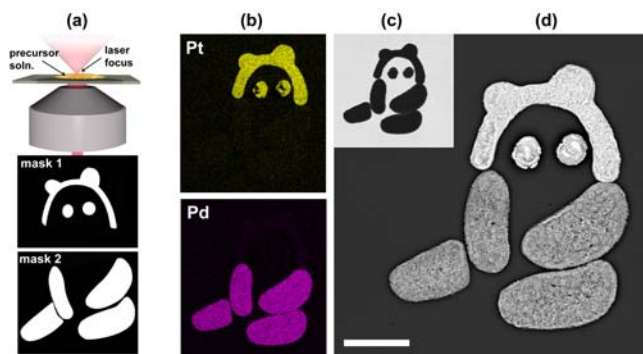
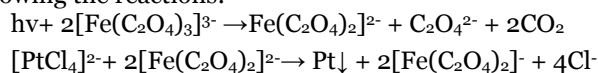


Figure 1. (a) Fabrication schematic showing the two digital masks used to define Pt and Pd. (b) EDS image maps indicating regions of Pt and Pd. (c) Bright field optical micrograph. (d) Backscatter SEM. Scale bar, 20 μm .

components which we envision can be applied broadly for site specific catalysis in microfluidic environments, for instance, toward the design and testing of catalytic micro-pumps and motors.¹³⁻¹⁷

The use of MPL to form conductive metallic structures has been explored,¹⁸⁻²¹ however, reports on MPL of catalytic materials are scant^{10,22} and the use of MPL to form Pt and Pd materials has not been reported. Previously, photoreduced Pt and Pd nanomaterials have been synthesized using methods often requiring the use of chemical stabilizers in order to generate nanoparticles or nanowires²³⁻²⁶. To adapt the synthesis of Pd and Pt nanocrystals for MPL conditions, we explored the use of precursors often used in platinotype/palladiotype photographic processes first developed in the late 19th century²⁷ and recently adapted by Jiang and Miller for fuel cell applications.^{28,29} In one such printing method, paper (serving as the support matrix) is embedded with $(\text{NH}_4)_2[\text{PtCl}_4]$, or $(\text{NH}_4)_2[\text{PdCl}_4]$ and $(\text{NH}_4)_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$ and exposed to UV light inducing photochemical reduction of the iron to form a strong reducing agent which can then reduce, for instance, Pt(II) to Pt(0) following the reactions:



To investigate MPL of Pt and Pd by adapting this photographic process, we mixed a 1:1 precursor solution comprised of 0.7 M of either the $(\text{NH}_4)_2[\text{PtCl}_4]$, or the $(\text{NH}_4)_2[\text{PdCl}_4]$ and 1.0 M of the iron (III) oxalate and tested Pt/Pd direct-writing using a mode-locked Titanium: Sapphire laser centered at 750 nm and focused upon a glass cover slip (Supporting Information). Using this procedure, Pt and Pd patterns could be printed sequentially on un-modified glass with arbitrary shapes and intrinsic registration using a scanning laser, dynamic-mask based approach (Figure 1a).¹² Bubbles were observed emanating from the opaque structure at the point of laser focus/fabrication, indicating solution boiling with likely contribution of evolution of CO_2 from ferric oxalate reduction (Supporting Movie 1). Structures could be rinsed rigorously post-fabrication without any detectable delamination or degradation. Panels (b) and (d) of Figure 1 show energy-dispersive X-ray spectrographs (EDS) and backscatter scanning electron micrographs

(SEM) respectively demonstrating the fabrication of well defined patterns of highly pure (i.e., no iron oxide contaminant detected with EDS) Pt and Pd.

The $(\text{NH}_4)_2[\text{PtCl}_4]$, $(\text{NH}_4)_2[\text{PdCl}_4]$ and $(\text{NH}_4)_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$ precursors display no significant absorbance above ~ 550 nm (Figure S1),²⁷ and excitation of the charge-transfer band of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$, which is required for its subsequent photolysis, is achieved in the range of $\sim 200 - 500$ nm.^{30,31} Thus, as expected, no initial deposition was observed when 5 mW continuous wave (CW) 750 nm light was employed. High resolution SEMs (Figure 2) show that the metallic patterns are comprised of small metallic granules, indicating that the rate of photoreduction within the focal volume is limited by the diffusion of metallic precursors.³²⁻³⁴ SEM cross-sectional analysis of an exemplary Pd structure revealed that the granular surface, in large part, is continuous throughout the structure interior down to the glass/metal interface at which point the structure appears solidified, indicating thermal melting/annealing at the interface—a consequence of heating via light absorption by the metallic pads. We estimated the steady state temperature rise (ΔT) at the laser focal point of the glass/metal interface using the solution for the low frequency limit (essentially CW) of the laser modulation:³⁵

$$\Delta T = \frac{A_0}{2\sqrt{\pi w_0 \Lambda}}$$

where A_0 is the average power (~ 5 mW) multiplied by the percentage of light absorbed by the metal at 750 nm ($\sim 30\%$ for Pt and Pd), w_0 is the $1/e^2$ radius of the focused laser spot (~ 350 nm), and Λ is the thermal conductivity of the glass ($1.3 \text{ W m}^{-1} \text{ K}^{-1}$) giving a maximum

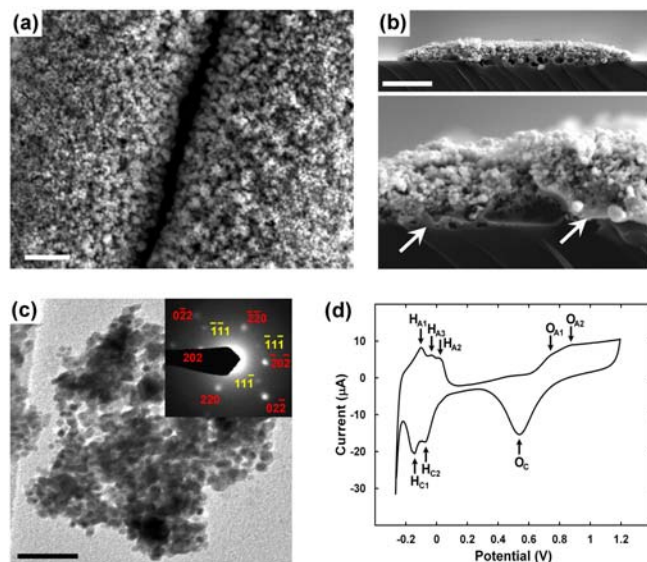


Figure 2. (a) Two Pd structures separated by a ~ 200 nm gap. Scale bar, 1 μm . (b) Cross section of a MPL-Pd line showing melting/annealing of the glass (left arrow) and Pd (right arrow). Scale bar, 5 μm . (c) TEM of MPL-Pt crystallites and electron diffraction pattern obtained from the edge of a cluster (corresponding to two crystallites). Scale bar, 50 nm. (d) CV of an MPL-Pt working electrode in 1.0 M H_2SO_4 shows hydrogen adsorption (cathodic peaks; Hc) and desorption (anodic peaks; Ha) and formation ($\text{Oa}_{1,2}$) and subsequent reduction (Oc) of an oxide layer.

steady state temperature rise of $\sim 930\text{K}$ under these conditions which is substantially higher than the annealing point for borosilicate cover glass (557°C).³⁶ Interestingly, we observed that further deposition of chemically and structurally identical Pt or Pd could be extended from an existing metallic structure using 750 nm CW laser light and the same precursor solutions; structures could not be deposited in this manner in the absence of the iron sensitizer. These observations indicate that the heat generated at the point of focus at the glass/metal interface leads to localized thermal decomposition/reduction of the ferric oxalate into an iron (II) reducing agent. The mechanism of metal oxalate thermal decomposition and resulting intermediates is highly dependent on experimental and environmental conditions³⁷ but extensive heating can result in the reduction of iron (III) to iron (II) with FeC_2O_4 as a possible intermediate.³⁸ FeC_2O_4 has also been shown to reduce platinum and palladium precursors salts.²⁷ Moreover, this mechanism provides an avenue to explore direct-writing of metals using widely available and less costly CW light sources.

Using our direct write set-up, we observed a reproducible minimum line width of ca. 2 μm , with gap width resolutions of ca. 200 nm (Figure 2a).³⁹ We characterized the electrical properties of MPL-Pt and Pd lines written on glass substrates using an *in situ* nanoprobe technique (Supporting Information) and measured resistivity values of 4.2 ± 0.5 and 2.3 ± 0.3 ($\mu\Omega\cdot\text{m}$) for Pt and Pd respectively which is approximately one order of magnitude higher than those for bulk metals. Further characterization of the crystallinity and electrochemical properties of MPL-Pt was carried out using transmission electron microscopy (TEM). TEM analysis of the MPL-deposited Pt scraped from glass substrates showed clusters with crystallites ranging in diameter from 4 - 8 nm (Figure 2c), and distinct crystallographic planes could be resolved in the electron diffraction pattern of crystallites located at cluster edges (Figure 2c inset). Cyclic voltammetry (CV) was used to characterize MPL-Pt (Figure 2 and Supporting Information) and we measured an electroactive surface area to geometric surface area ratio of ~ 36 .

The emerging field of synthetic catalytic nanomotors and pumps provides an exciting testbed to explore nanomaterials with life-like energy conversion strategies.^{5-7,40} To achieve the work necessary to directionally power such devices generally requires asymmetric placement of the catalyst in relation to the surrounding environment in order to generate net directional motion and flow.^{16,17,41} MPL enables arbitrary 3D structures to be readily designed and fabricated allowing functional/asymmetric geometries to be rapidly prototyped. We explored Pt catalyzed decomposition of hydrogen peroxide to generate directed fluid and particulate flow within 3D micro-chambers and channels. In Figure 3a, a Pt pad was patterned onto glass and then encased within a photo-crosslinked protein chamber containing a self-crossing spiral outlet. Addition of 1% H_2O_2 resulted in continuous and directed flow of oxygen through the spiral (Supporting Movie 2) as the peroxide substrate could be replenished at the catalytic site, for the most part, via diffusion across the

protein hydrogel chamber walls and ceiling thereby allowing the majority of the spiral channel to maintain constant O_2 pressure. In contrast, directing the oxygen outflow into an asymmetric channel (Figure 3b) resulted in a peristalsis-like effect on the channel, with the channel fluid periodically compressed and released by the oxygen bubble evolution and resultant negative pressure developed upon outflow. Pumping is illustrated by the directional transport of microspheres at relatively high velocities (up to ca. 60 $\mu\text{m s}^{-1}$) through the channel (Figure 3b and Supporting Movie 3). Importantly, this approach offers greater flexibility versus existing techniques^{15,17} in the design of autonomously powered microfluidics.

Finally, we explored Pt patterning within a preformed 3D microenvironment. Unfortunately, formation of metallic pads on protein substrates resulted in deformation of the protein support. However, this challenge was overcome by developing a silica composite⁴² which provided sufficient mechanical reinforcement of the structural surfaces defined by the protein template to withstand the subsequent heat generated during metal deposition. We designed a geometry where gas flow is forced downward, underneath the catalyst, to exit into the surrounding fluid (Figure 3c). Traversing the imaging plane through the structure shows that the gas generated from the top chamber is directed underneath the Pt catalyst (Supporting Movie 4), demonstrating high resolution integration of a metallic component that is otherwise unachievable without 3D lithographic control.

We have demonstrated that MPL of Pt and Pd facilitates the design of dynamic microsystems based on harnessing localized catalysis within 3D

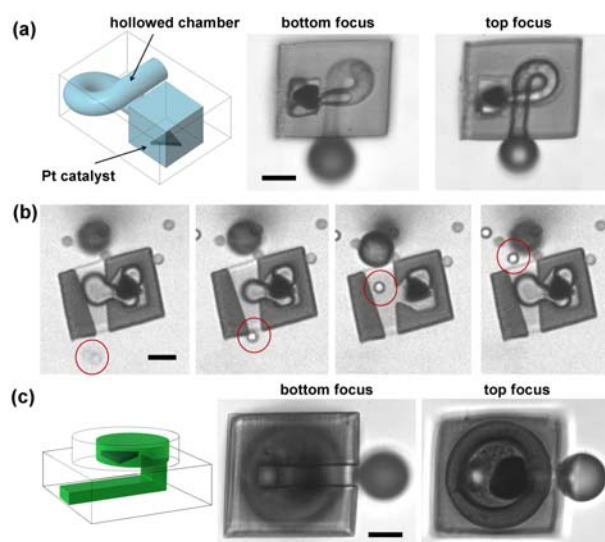


Figure 3. (a) A Pt catalyst contained in a protein chamber directs gas through a self-crossing spiral channel. (b) The directional outflow of gas produced at an MPL-Pt catalyst contained in a microchamber pumps a 5 μm particle (circled in red) through the asymmetric channel over approximately 1 second. (c) An MPL-Pt catalyst printed inside the upper chamber of a 3D microchamber directs gas flow downwards underneath the catalyst. Scale bars, 10 μm .

microenvironments to generate directed fluid and gas flow. These autonomous pumps and fluidics may be useful for flow generation, fluid mixing, propulsion, collection and transport. Additionally MPL-Pt and Pd materials display excellent electronic and catalytic functionality; further enhancement is expected by exploring alloyed systems and controlling resolution and particle morphology using structure-directing agents.^{1,32,43,44} or electroplating techniques.³⁴ Fabrication of Pt and Pd structures with free-form, 3D architectures is currently being investigated through judicious variation of the chemical and environmental parameters in an effort to overcome the low structure fidelity incurred via laser heating.^{18,19,32} The ability to prototype arbitrary 3D microscale electroactive and catalytic surfaces provides a new toolset with which to fabricate dynamic, 3D nano/microscale systems.

ASSOCIATED CONTENT

Experimental protocols, resistivity and electrochemical analysis are provided in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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